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THE SORPTION OF CHLOROPHENOLIC COMPOUNDS TO PRIMARY CLARIFIER SOLIDS

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ABSTRACT

An experimental study of the aqueous retention of chlorophenolic chemicals by wood fibers and sludge samples indicates the hydrophobic sorption to the lignin fraction of clarifier solids is responsible for the organic chemical retention by primary sludge. Measurements of the sludge/water distribution coefficient for a model system involving the aqueous sorption of 2,4-dichlorophenol and 2,4,5-trichlorophenol to kraft softwood fibers showed a strong dependency on the compound's octanol-water distribution coefficient and on the kappa number of the fibers. Experiments also indicate chlorophenolic compounds do not bind to fiber-derived solids when they are in their conjugate base or ionized form. Through sorption measurements of model compounds using collected clarifier sludge and overflow samples, these findings are confirmed for the various fibrous components of primary sludge. The results indicate the sludge/water distribution for chlorophenolic molecules will be limited by their ionization under the alkaline conditions of primary treatment, but for compounds not possessing acidic groups, hydrophobic sorption can result in a strong magnification of concentrations in the sludge.

INTRODUCTION

Influents from pulping and bleaching operations contain fibrous solids and a variety of residual organic chemicals (1-5). Depending on the extent to which these compounds sorb to influent solids, the removal of sludge at the primary clarifier can potentially concentrate high levels of hydrophobic chemicals. Studies on the aqueous sorption of chlorophenolics to a variety of materials including soils, sediments, and biophases show that they have a tendency to concentrate in the solid phase as a result of their aversion to water (6-11). This "hydrophobic" sorption is typically measured in terms of a distribution coefficient, K_d. For the distribution of a specific compound, K_d is defined as the equilibrium ratio between the concentration that binds to the solid phase to the concentration which remains in the water, i.e.,

$$K_d = \frac{\text{Concentration in Solids}}{\text{Concentration in Water}} \quad (1)$$

For the primary sludge/water distribution of chlorophenolics, a large K_d indicates a greater tendency to be carried with the sludge.

Because of the fibrous nature of primary sludge (12), the sludge/water distribution coefficient is, in essence, a fiber/water distribution coefficient. A study recently completed in our laboratories on the retention of two model compounds (2,4-dichlorophenol and 2,4,5-trichlorophenol) by pulp fibers examined the effects of various chemical and physical variables on the sorption process. Di- and trichlorinated chlorophenols were chosen for the study because of their stability, and the current trend toward chlorine dioxide bleaching which has been shown to produce less highly chlorinated residual products (13,14). The study generated important information about the dependency of K_d on the concentration of chlorophenols and the chemical components of fibrous solids. It also reinforced the importance of the hydrophobicity of a compound in determining its retention.

The most prominent finding of our experiments was the dominance of lignin in the sorption process. Experiments using fibers, cotton linters, and model lignin particles show the sorption by lignin to be more than two orders of magnitude higher than that for cellulose. Assuming a hydrophobic-driven mechanism, this difference is not surprising given the strong interaction that exists between cellulose and water. Studies also indicate that chlorophenol retention is limited to the neutral form of the compound when ionization is possible. This is assumed to be caused by the ionized compound's greater compatibility with water due to the negative charge (i.e., charging allows the compound to interact with water). Figure 1, which plots the distribution coefficient for the retention of 2,4,5-trichlorophenol to kappa number 105 softwood fibers as a function of pH, demonstrates the dominance of the chlorophenol's neutral form in the sorption to fibers. Figure 2 plots the sorption of 2,4,5-trichlorophenol to model lignin particles, 105 kappa number softwood pulp, and cotton linters as a function of ionization. This again demonstrates that the neutral compound is preferentially sorbed. It also shows the dominance of lignin in the retention process. Based on these results, K_d for the fiber/water distribution of chlorophenols can be written as,

$$K_d = \begin{pmatrix} \text{Mass} \\ \text{Fraction} \\ \text{Lignin} \end{pmatrix} \times \begin{pmatrix} \text{Fraction of} \\ \text{Compound in} \\ \text{Neutral Form} \end{pmatrix} \times \begin{pmatrix} \text{Distribution} \\ \text{Coefficient} \\ \text{for Lignin} \end{pmatrix} \quad (2)$$

The application of this equation to primary sludge suggests that only the lignin (from fibers, shives, and precipitates) is significant in determining chlorophenolic retention. Because of the difficulty in gauging the lignin content of sludge, as well as changes in lignin's sorption behavior due to its oxidation from bleaching, the equation can only be used qualitatively. But, it does provide insight on the importance of sludge lignin content, clarifier pH, and compound pK_a values in determining retention.

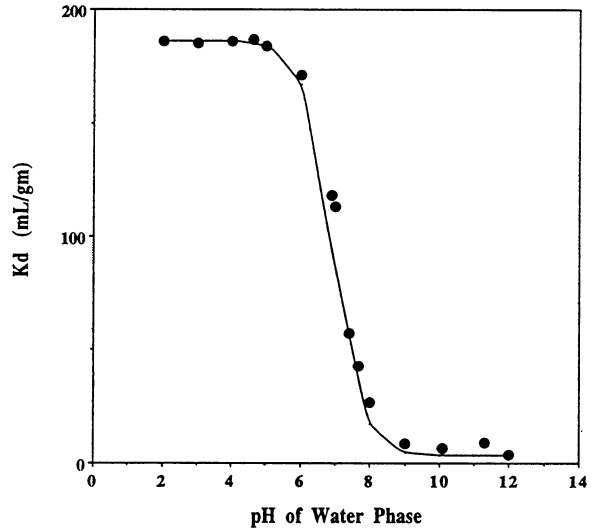

Fig. 1. Sorption of 2,4,5-trichlorophenol to 105 kappa number softwood fibers.

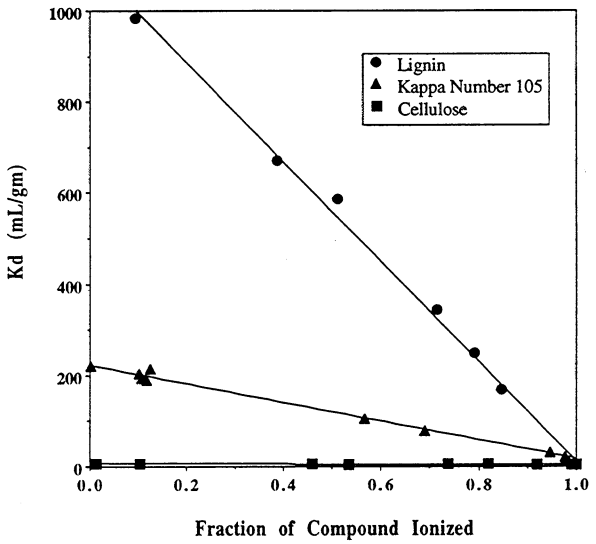

Fig. 2. Sorption of 2,4,5-trichlorophenol to lignin precipitates, 105 kappa number fibers, and cotton linters.

Other results of importance to the sludge/water distribution of chlorophenolics from the model system are concentration and ion effects. Experiments show linear fits of sorption isotherms at the low concentrations typical of bleach plant influents. Isotherm studies also show no impact from the presence of other chlorophenolic materials well into ppm concentrations (i.e., no competitive sorption). The inorganic load on the other hand does tend to increase organic retention by fibrous solids. Ion titration measures of clarifier overflow samples indicate that the concentration of the dominant ions (chloride and sulfate) is about 800 ppm. At these levels, the increase in sorption is expected to be modest. But, it should be noted that trends toward greater mill closure will cause ion levels to significantly increase which may result in much higher K_d values for all organic molecules.

EXPERIMENTAL

A primary sludge sample and a clarifier overflow sample (extractive filtrates only) were obtained from a 100% chlorine dioxide substitution bleached kraft mill. Small amounts of formalin were added to both solid and aqueous effluents to quench all biological activity, and the samples were stored at 5°C. A portion of the overflow sample was passed through a 0.05 μm polycarbonate filter (Poretics, Livermore, CA) from a pressurized stir cell (40 psi) and sent to Ecology and Environment, Inc. (Lancaster, NY) for ion analysis. Both [^{14}C] 2,4-dichlorophenol (8.42 mCi/mmol) and [^{14}C] 2,4,5-trichlorophenol (4.40 mCi/mmol) were stored in amber vials as methanol solutions at 2°C. 2,4-Dichlorophenol was > 98% pure and 2,4,5-trichlorophenol was > 99% pure as determined by HPLC.

Experiments on sludge included studies with whole sludge and sludge separates (fibers, shives) in either clarifier overflow or pH 7 buffered distilled water. In the study of sludge with the shives removed, the fibers were run either unwashed or after a thorough washing with a pH 9 buffer solution to remove fines and other organic debris. The general procedure for these experiments was to mix a 100 ppb solution of either [^{14}C] 2,4-dichlorophenol or [^{14}C] 2,4,5-trichlorophenol with the sludge samples in 20 mL amber vials capped with Teflon-lined seals. The samples were mixed for 24 hours, and sorption was determined by the loss of activity from the aqueous phase. All mass balances indicate > 95% recoveries.

Influent fines were isolated by centrifuging clarifier

overflow samples to produce a 500 mg/L solids concentration. A measurement of the solids level of each 500 mL sample was determined by separating the fines from 10 mL aliquots by vacuum filtration through a preweighed 0.01 μm anodized aluminum filter (Alltech, Deerfield, IL). A seven fold solids level determination from each of the generated solutions indicated good reproducibility. FTIR measurements on the recovered fine material indicate it is composed largely of fibrous debris (high levels of both cellulose and lignin). K_d values for the samples were measured by adding either [^{14}C] 2,4-dichlorophenol or [^{14}C] 2,4,5-trichlorophenol to produce a 100 ppb solution, stirring the system for 24 hours, and running liquid scintillation counting on the fines removed through the filtration of 10 mL aliquots. Isotope recoveries were > 99%.

RESULTS AND DISCUSSION

Table 1. Log K_{ow} and pK_a values for model compounds and ranges for several chlorinated phenolic compounds. Log K_{ow} and pK_a for model compounds are experimental values (1[a], and measured[b]). The ranges are based on both available experimental and predicted values (15).

Compound	Log K_{ow}	pK_a
2,4-Dichlorophenol	3.20[a]	7.87[b]
2,4,5-Trichlorophenol	3.72[a]	6.92[b]
6-Chlorovanillin	1.5-2.0	7.5-8.6
5-Chlorovanillin		
2-Chlorosyringaldehyde		
4,5-Dichlorocatechol	2.2-2.7	7.0-8.6
3,4-Dichloroguaiacol		
4,5-Dichloroguaiacol		
5,6-Dichlorovanillin		
2,6-Dichlorosyringaldehyde		
2,4,6-Trichlorophenol	3.0-3.5	7.0-7.75
3,4,5-Trichlorocatechol		
3,4,5-Trichloroguaiacol		
4,5,6-Trichloroguaiacol		
Trichlorosyringol		
Tetrachlorocatechol	3.7-4.0	6.0-7.0
Tetrachloroguaiacol		

Table 1 lists the log of the octanol/water distribution coefficients (log K_{ow}) and pK_a values for the model compounds and general ranges for several other phenolic molecules. Because octanol interacts very little with nonpolar and semipolar organic compounds (like chlorophenols), the distribution of an organic between octanol and water is believed to be driven by the compound's aversion to water. Thus, the log K_{ow} value for an organic molecule provides a relative measure of its hydrophobicity. As a general rule, compounds with a log $K_{ow} > 2$ are considered to be hydrophobic. The table shows most chlorophenolics have log k_{ow} values in the 2 to 3 range which corresponds to a low to moderate hydrophobicity. The listed values also demonstrate the increased hydrophobicity which accompanies increased chlorination for the phenolics (e.g., 2,4,5-trichlorophenol is more hydrophobic than 2,4-dichlorophenol). This is because chlorine atoms increase the size of a compound without significantly increasing its ability to interact with water.

The pK_a values are also affected by the presence of chlorine. The chlorine atoms tend to stabilize a negative charge and, therefore, promote ionization. This is evident from the decreasing pK_a values that accompany increased phenolic chlorination. As discussed and demonstrated (Fig. 1) in the introduction, the ionization of a compound will dramatically effect its sorption to fibrous solids by eliminating the hydrophobic driving force. Thus, the increased presence of chlorine atoms on chlorophenolic compounds can have the opposing effects of raising the hydrophobicity of its neutral form while decreasing the compounds overall hydrophobicity through ionization.

Table 2. The distribution of model compounds between sludge and sludge components and distilled water at a pH of 7.00 ([a]except for the fines which were run in the clarifier overflow solution at an adjusted pH of 7.00).

	K_d(mL/gm)	
	2,4-DCP	2,4,5-TCP
Whole Sludge	68.6 ± 12.1	112 ± 19.7
Shives	101 ± 6.21	146 ± 5.51
Unwashed Fibers, Shives Removed	61.7 ± 8.34	101 ± 10.9
Washed Fibers, Shives Removed	28.4 ± 5.97	43.4 ± 4.41
Fines[a]	201 ± 6.41	331 ± 7.42

The effects of hydrophobicity and the dominance of lignin in retaining chlorophenolics are demonstrated by the sorption of model compounds to the various components of sludge (Table 2). As was noted, the neutral form of trichlorophenol is more hydrophobic than the neutral form of dichlorophenol. A comparison of sorption for these compounds for the various sludge components indicates this increased

hydrophobicity leads to higher K_d values. The differences are somewhat tempered by the ionization of 2,4,5-trichlorophenol at a pH of 7.00 (> 50% ionized), but remain significant. The role of lignin in sorption is demonstrated by the variation of K_d which accompanies the different sludge separates. The fines have the greatest sorption which would be expected due to their high lignin content. The shives which also have a high lignin content are next, followed by the fibers, and finally, the washed fibers. Although the washing did not remove all of the organic debris, it did drop the fiber sorption by more than 50%. This indicates that the fines rather than the fibers are responsible for the chlorophenol retention by unwashed fibers. The results reinforce the hypothesis that lignin is the primary carrier of retained hydrophobic molecules in sludge.

Table 3. Results for the distribution of model compounds between primary sludge and clarifier overflow solution at a pH of 7.77.

	K_d (mL/gm)
2,4-Dichlorophenol	41.0 ± 6.14
2,4,5-Trichlorophenol	33.1 ± 5.72

Table 3 lists the measured K_d values for the distribution of model compounds between the collected sludge and clarifier overflow. These samples were run to demonstrate the extent of sorption that occurs under the conditions typical for the primary clarifier. Again, the effects of ionization in reducing hydrophobic sorption are evident. In this case, the more hydrophobic 2,4,5-trichlorophenol (log K_{ow} = 3.72) has a lower sorption than 2,4-dichlorophenol (log K_{ow} = 3.20) due to greater ionization. At a pH of 7.77, 2,4,5-trichlorophenol (pK_a = 6.92) will mostly be in its charged form, while less than 50% of 2,4-dichlorophenol (pK_a = 7.87) will be ionized. Rough estimates for the sorption of other chlorinated phenolic compounds based on comparisons of their log K_{ow} and pK_a values with those for the model compounds indicate the sorption of these compounds to whole sludge under clarifier conditions (pH 7.8-8.0) will be in the range of about 1 to 50 mL/gm. It appears K_d is limited by low pK_a values (i.e., ionization) for the tetrachlorinated compounds, and by the low hydrophobicities for the monochlorinated compounds. This leaves the di- and trichlorinated compounds with the highest estimated K_d values. It is interesting to note that in the absence of ionization, the predicted sorption of these compounds would be very high. For example, the K_d predicted for 2,4,5-trichlorophenol at the clarifier if it were not ionized would be close to 300 mL/gm.

In summary, the experiments indicate lignin is the dominant carrier of residual organic compounds from pulping and bleaching operations. For collected whole sludge samples, the lignin retention translated into chlorophenolic sludge concentrations that are about an order of magnitude above that in the clarifier overflow waters. Phenolic sorption appears to be controlled by the compound's hydrophobicity which increases with chlorination and dramatically falls with ionization. For organic structures that do not contain an ionizable acid group, sorption, unrestricted by ionization, will climb strongly with the compound's hydrophobicity. Estimates of the sludge/water distribution of neutral compounds indicate sludge concentrations can climb to many orders of magnitude above their levels in the bleaching influents.

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